

Studying on The Removal of Pb(II) using Fire Clay – TiO₂ Nanocomposite and Fire Clay

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Abstract

The present study was aimed at investigating the adsorption behavior of Pb(II) ions onto Fire Clay-TiO₂ nanocomposite (NC) and Fire Clay (FC). The effect of several parameters such as adsorbent dose, contact time, initial concentration, pH and temperature has been studied. The adsorption followed pseudo second order, Elvovich kinetic models. Intraparticle diffusion model has also been attempted. The adsorption of Pb(II) was found to be maximum in the pH range 7-10.5. Adsorption on both clay and nanocomposite obey Langmuir, Freundlich model. The thermodynamic parameters ΔG° , ΔH° and ΔS° have also been evaluated. Adsorptions on both clay and nanocomposite were found to be exothermic and chemisorptive in nature. Chromium removal was better with nanocomposite than with clay.

Keywords: Adsorption isotherm; Fire Clay; Fire Clay-TiO₂ nanocomposite; Heavy metal.

1. INTRODUCTION

Water pollution is the major problem in the global context. The pollution of water occurs when harmful substances are released into the water in large quantities and the devastating effects of the effluents let out from dyeing, textile, leather making, pharmaceutical, food processing, cosmetics, paper and other industries are well known.

Synthetic organic dyes are widely used in textile industry due to their high solubility and large tinctorial value (Ho and McKay, 1999). The presence of these dyes in waste waters was a matter of great concern to all since they are non-biodegradable, toxic and carcinogenic (Öztürk and Malkoc, 2014). Industrial waste waters, if they contain heavy metals like lead, copper, nickel, cadmium and chromium, if not properly treated, cause serious environmental pollution imposing costly clearing operations (Babu and Ramakrishnan, 2003). Active research is being carried by researchers all over the world to find ways and means to remove the harmful pollutants from waste water before discharging them into the main streams.

During the past three decades, several physical, chemical and biological methods have been reported for treating effluents containing dyes and heavy metals. The methods like coagulation, flocculation, ion-exchange, membrane separation, oxidation, adsorption etc., have been tried. Among these numerous techniques, adsorption was identified as a viable method, as other methods have

the disadvantages like huge sludge production, high cost, technical difficulties, handling and disposal problems. If the adsorption system is designed correctively it will produce high quality treated effluents. Commercial activated carbon was the most opted adsorbent because of its excellent adsorption capacity. But owing to the high cost involved, attempts have been made, in recent years to find inexpensive alternate adsorbents. This led to the discovery of several natural materials, plant products, agricultural and industrial wastes that could be utilized as alternatives to commercial activated carbon. Numerous materials such as coal, perlite, alunite, clay materials (montmorillonite, rectorite, vermiculite, kaolinite etc.) activated slag and agricultural wastes (bagasse pith, maize cob, rice husk, waste fruit residues etc) (Mall, 2005; Mehmet Doğan *et al.* 2000; Parimaladevi and Venkateswaran, 2011) have been tried as adsorbents.

2. MATERIALS & METHODS

Fire Clay (3 g) was allowed to swell in 15 mL of water-free alcohol and stirred for 2 hrs at 25 °C to get a uniform suspension. At the same time, the titanium dioxide (3 g) was dispersed into water-free alcohol (15 mL). Then the diluted titanium dioxide was slowly added into the suspension of Fire Clay and stirred for a further 5 hrs at 25 °C. Finally, 5 mL alcohol mixed with 0.2 mL deionized water was slowly added. The stirring was continued for another 5 hrs at 25 °C and the resulting suspension kept overnight in a vacuum oven for 6 hrs at 80 °C.

2.1 Adsorbate solution

A stock solution of Pb(II) was prepared by dissolving 1.599 g of Lead Nitrate (99.9%) in 1000 mL of doubly distilled water.

2.2 Characterization of adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD pattern of pure fire clay Fig. 1 and that of fire clay-TiO₂ nanocomposite Fig. 2 show characteristics peaks at 28° and 30° which confirm the presence of fire clay-TiO₂ phase in the nanocomposite. The surface morphology of the adsorbent was visualized via scanning electron microscopy (SEM) Fig. 3 and Fig. 4. The diameter of the composite range was 50 µm.

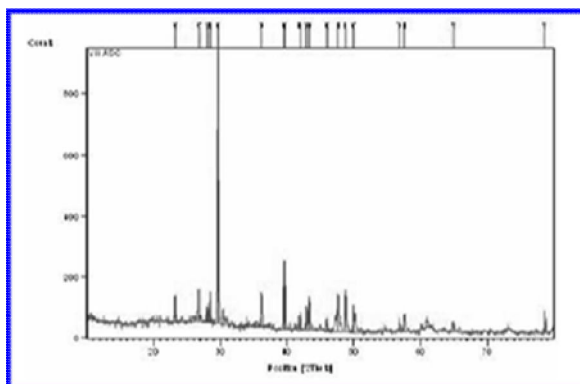


Fig.1: XRD analysis of fire clay

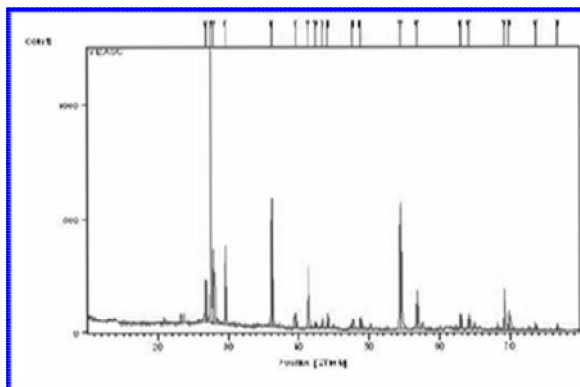


Fig. 2: XRD analysis of Fire Clay+ TiO₂ nanocomposite

2.3 Batch adsorption experiments

Batch adsorption experiments were conducted by agitating the flasks for a predetermined time intervals in a thermostat attached with a shaker at a desired temperature. Adsorption isotherm study was carried out with different initial concentrations of Pb(II) ranging from 10 to 40 mg/L while maintaining the adsorbent dosage at 0.1 g. The effect of contact time and pH was studied with Pb(II) concentration of 10-40 mg/L and an adsorbent dosage of 0.1 g. The solution pH was adjusted in the range of 5-11 by using dilute hydrochloric acid and sodium hydroxide solutions. Experiments were carried

out by varying the adsorbent amount from 0.1 to 1.0 g with Pb(II) concentration ranging from 10 to 40 mg/L. The concentration of free Pb(II) ions in the effluent was determined spectrophotometrically by developing a dark red color using NH₄Cl and ammonia buffer solution.

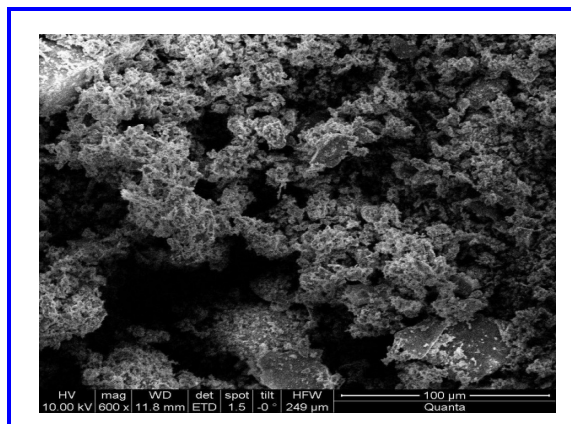


Fig. 3: SEM of pure Fire Clay

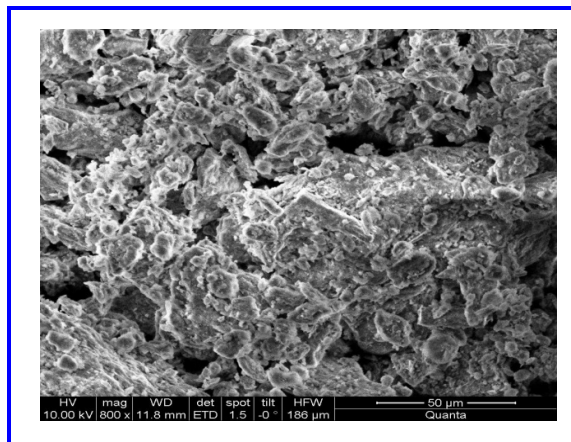


Fig. 4: SEM of Fire Clay + TiO₂ Composite

3. RESULTS & DISCUSSION

3.1 Effect of adsorbent dose

The effect of adsorbent dose on Pb(II) removal was studied by keeping all other experimental conditions constant except that of adsorption dose. The results showed that with increase in adsorbent concentration there is a decrease in the amount adsorbed per unit mass of the adsorbent for both clay and nanocomposite Fig. 5 and Fig. 6. This may be basically due to adsorption sites remaining unsaturated during the adsorption process.

3.2 Effect of contact time and initial metal concentration

The effect of contact time and different initial concentrations has been studied using both clay and nanocomposite. It is observed that in both cases the percentage removal of Pb(II) ions increase with increase

in metal ion concentration Fig. 7 and Fig. 8 and attains saturation in 50 to 135 min with nanocomposite and 60 to 150 min with clay. The removal rate by adsorption is rapid initially, gradually decreases with time and finally attains equilibrium is rapid initially.

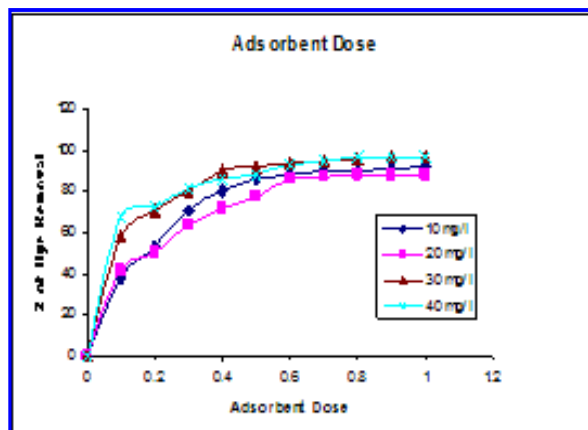


Fig. 5: Effect of adsorbent dose of Fire Clay + TiO_2 Nanocomposite

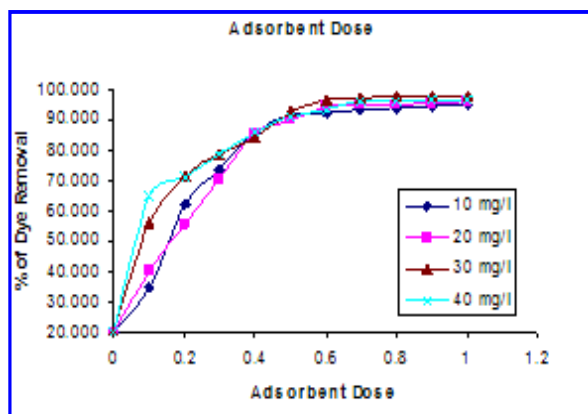


Fig. 6: Effect of adsorbent dose of Fire Clay

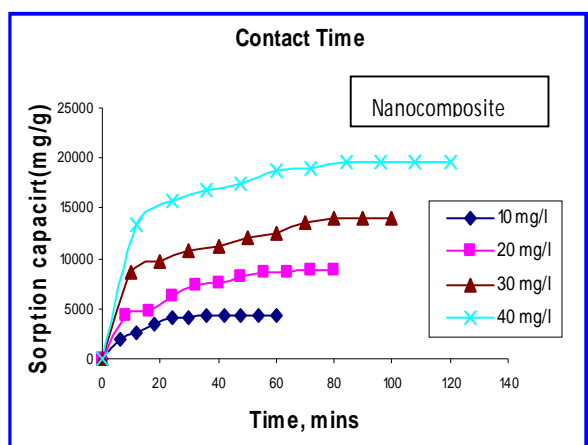


Fig. 7: Effect of contact time and initial metal concentration of Fire Clay+ TiO_2 Nanocomposite

3.3 Effect of pH

Adsorption of Pb(II) was studied at various pH values and results are depicted in Fig. 9 and Fig. 10. The initial pH of solution was varied from 5 to 11 with the adsorbate concentration varying from 10-40 mg/L maintaining the adsorbent dose at 0.1 g and the contact time as 90 mins for both clay and nanocomposite.

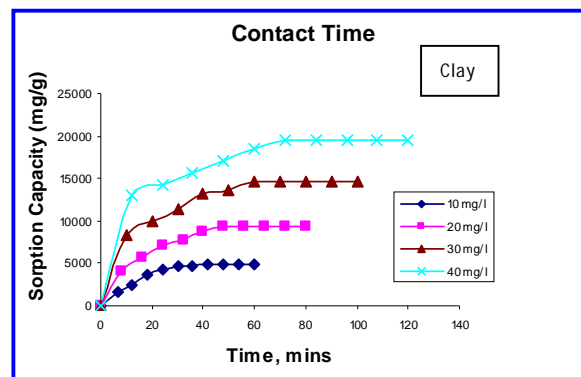


Fig. 8: Effect of contact time and initial metal concentration of Fire Clay

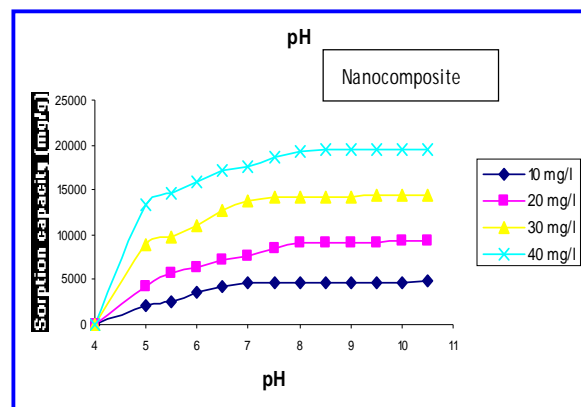


Fig. 9: Effect of pH of Fire Clay + TiO_2 Nanocomposite

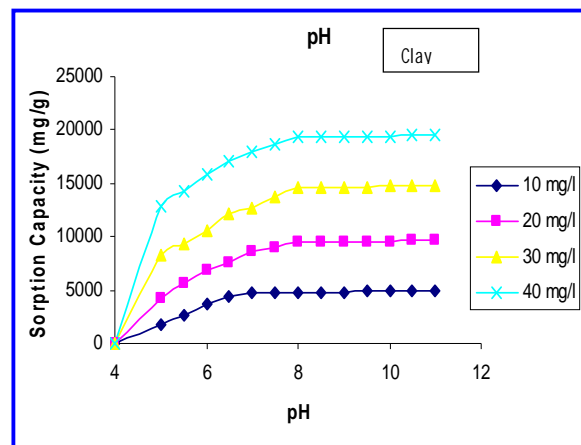


Fig. 10: Effect of pH of Fire Clay

From this figures it is clear that lead adsorption efficiency is highest at pH 7-10 with nanocomposite and at 6-10 with clay. pH_{zpc} for the nanocomposite and clay was determined as 8.0.

3.4 Effect of temperature

Effect of temperature on adsorption of Pb(II) ion was studied at different temperatures viz., 303, 307, 311, 315K and the results are shown in Fig. 11 and Fig. 12. It is observed that adsorption of chromium ions increases (Kobya *et al.* 2000) with increasing temperature showing the process to be endothermic with both adsorbents.

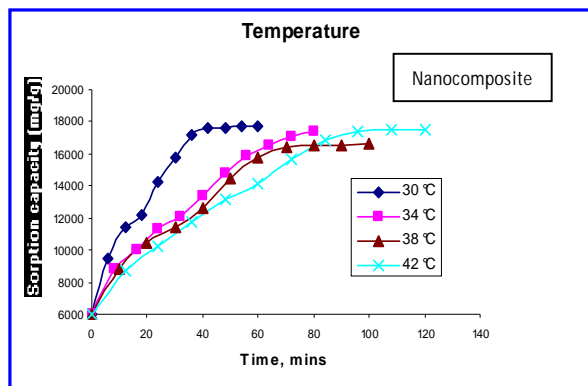


Fig. 11: Effect of Temperature of Fire Clay + TiO₂ Nanocomposite

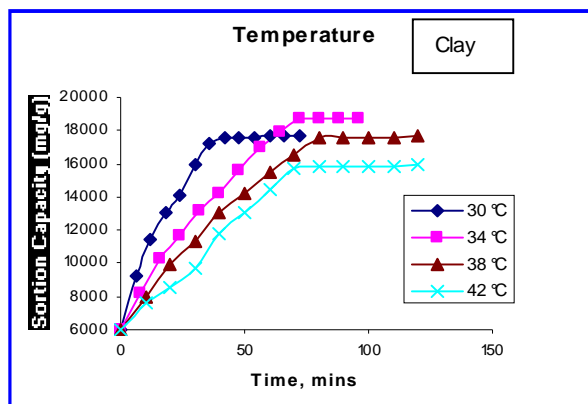


Fig. 12: Effect of temperature of Fire Clay

3.5 Adsorption isotherm

3.5.1 Langmuir adsorption isotherm

The Langmuir isotherm model commonly used for the adsorption of a solute from a aqueous solution (Langmuir, 1916) in its linear form can be represented as

$$C_e / q_e = i / b q_0 + C_e / q_0 \quad (1)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/L) and q_0 and 'b' is Langmuir constants related to adsorption capacity and rate of adsorption respectively. As required by equation (1), plotting C_e/q_e against C_e gave a straight line, indicating that the adsorption of heavy metal on both clay and nanocomposite follow the Langmuir isotherm Fig.13 and Fig. 14. The Langmuir constants 'b' and q_0 were evaluated from the slope and intercept of the graph.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which is defined by,

$$R_L = 1 / (1 + b C_0) \quad (2)$$

Where, C_0 is the initial solute concentration, 'b' the Langmuir adsorption constant (L/mg). R_L value less than one indicates favourable adsorption (Norrozi *et al.* 2007). The R_L values shown in table1 (all<1) confirm that the adsorption of Pb(II) follow Langmuir isotherm.

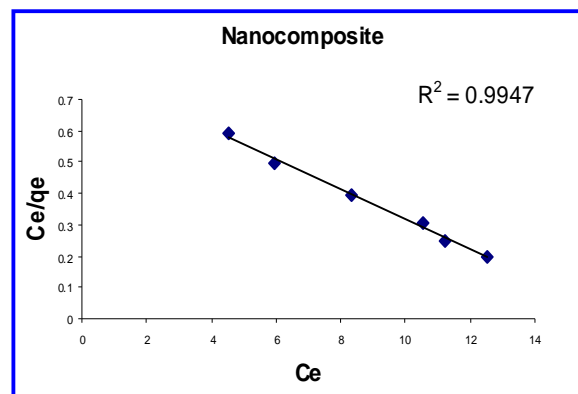


Fig. 13: Langmuir Adsorption Isotherm of Fire Clay + TiO₂ Nanocomposite

Table 1: The values of Langmuir constant Q^0 and b in addition to R_L

Conc. of metal mg/L	R_L	Q^0	b	R^2	R_L	Q^0	b	R^2
20	0.9966	9.49	0.022	0.9947	0.9956	8.74	0.0017	0.9909
40	0.9932				0.9912			
60	0.9899				0.9869			
80	0.9865				0.9827			
100	0.9832				0.9784			
120	0.9800				0.9742			

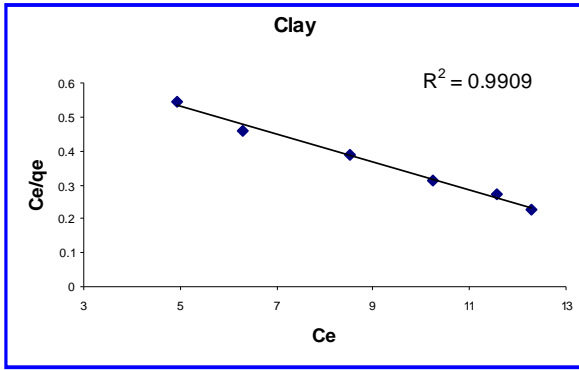


Fig. 14: Langmuir Adsorption Isotherm of Fire Clay

3.5.2 Freundlich model

The Freundlich isotherm, in its logarithmic form can be represented as

$$\log q_e = \log K_f + 1/n \log C_e \quad (3)$$

Where K_f and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate. The plot of $\log q_e$ versus $\log C_e$ gave straight lines with good regression coefficients indicating that the adsorption of heavy metal follow the Freundlich isotherm Fig. 15 and Fig.16. The values of K_f and $1/n$ calculated from the intercept and slope respectively are recorded in Table 2.

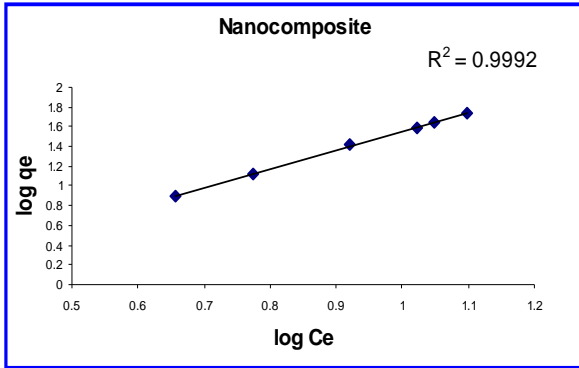


Fig. 15: Freundlich Isotherm of Fire Clay + TiO₂ Nanocomposite

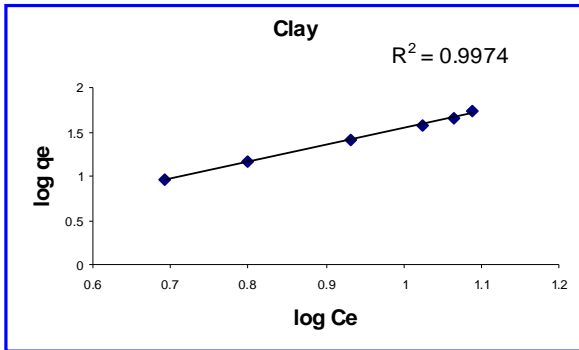


Fig. 16: Freundlich Isotherm of Fire Clay

Table 2. The values of Freundlich constant K_f and n

Adsorbent	K_f (L/mg)	n (mg/g)	R^2
Fire Clay-TiO ₂ nanocomposite	6.025	1.96	0.9992
Fire Clay Clay	5.80	1.95	0.9974

3.6 Adsorption kinetics

In order to investigate the mechanism of adsorption of chromium by the nanocomposite and clay pseudo first order, pseudo second order and Elvovich model were considered. It is observed that the data for Pb(II) on both Fire Clay+TiO₂ nanocomposite and Fire Clay does not fit into pseudo first order kinetics.

3.6.1 Pseudo second order kinetics

In linearised form the pseudo second order kinetic model can be represented as

$$t/q_t = 1/k_2 q_e^2 + 1/q_e \times t \quad (4)$$

Where k_2 is the second order rate constant (g/mg min). A plot of t/q_t and 't' should be linear. q_e and k_2 can be calculated from the slope and intercept of the plot. The linear plots Fig.17 and Fig.18 obtained for the adsorption of Pb(II) on the nanocomposite and clay at various metal ion concentrations clearly show that the adsorption process to follow pseudo second order.

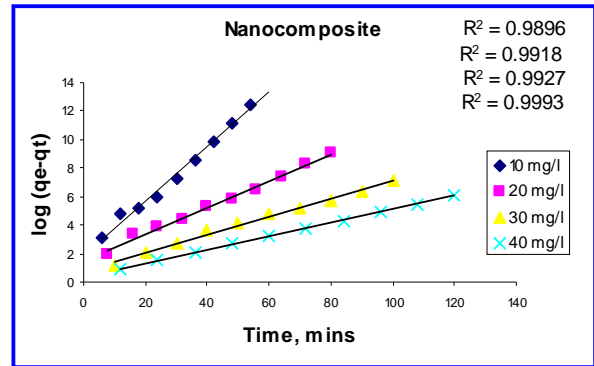


Fig. 17: Pseudo second order Adsorption kinetics of Fire Clay+ TiO₂ Nanocomposite

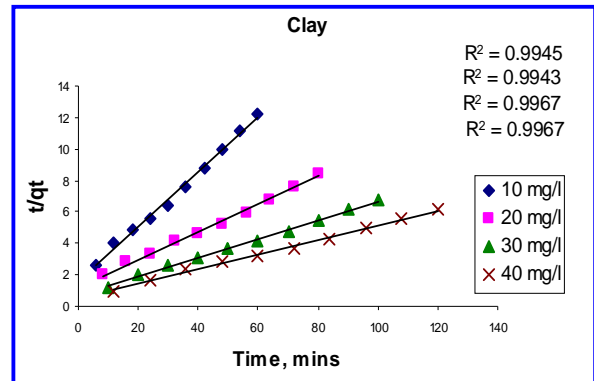


Fig.18: Pseudo second order Adsorption kinetics of Fire Clay

3.6.2 Elkovich kinetic model

The Elkovich equation which is mainly applicable for chemisorption and often valid for systems with heterogeneous adsorbing surfaces (Karthikeyan *et al.* 2005) is generally expressed in its integrated form as

$$Q_t = (1/b) \ln(ab) + (1/b) \ln t \quad (5)$$

Where 'a' is the initial adsorption rate (mg/g min) and 'b' is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q_t vs $\ln t$ should be linear with slope $1/b$ and intercept $\log 1/b \ln(ab)$. Fig. 19 and Fig. 20 show that the plots are linear over a wide range as expected suggesting chemisorptions.

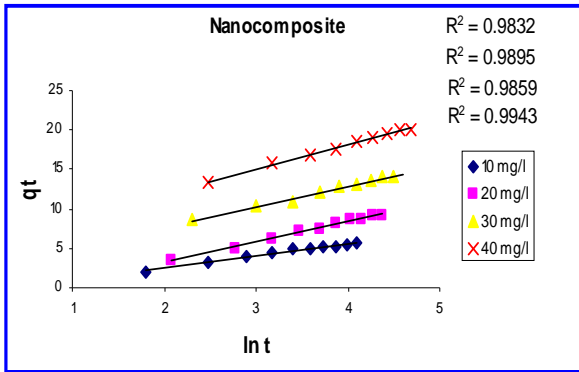


Fig. 19: Elkovich kinetics of Fire Clay + TiO₂ Nanocomposite

3.7 Weber-Morris intraparticle diffusion model

A graphical method to prove the occurrence of intra-particle diffusion and to determine if it was the rate determining step in adsorption process was introduced by Weber and Morris (Ozcan *et al.* 2005; Weber and Morris, 1963). Intra-particle diffusion was characterized using the relationship between specific sorption (q_t) and the square root of time ($t_{1/2}$) as

$$q_t = K_{id} t_{1/2} + C \quad (6)$$

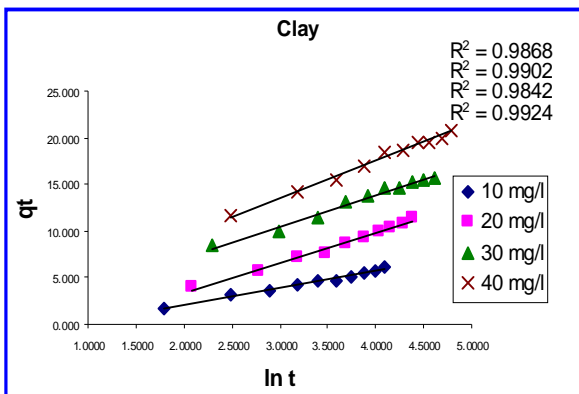


Fig. 20: Elkovich kinetics of Fire Clay

Where q_t is the amount adsorbed per unit mass of adsorbent (mg/g) at time 't' and ' K_{id} ' is the intraparticle diffusion rate constant. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin suggesting that pore diffusion is the only controlling step and not the film diffusion Fig. 21 and Fig. 22.

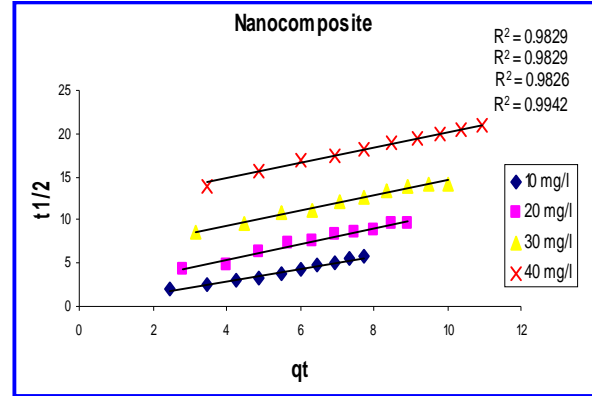


Fig. 21: Weber-Morris Intraparticle Diffusion model of Fire Clay + TiO₂ Nanocomposite

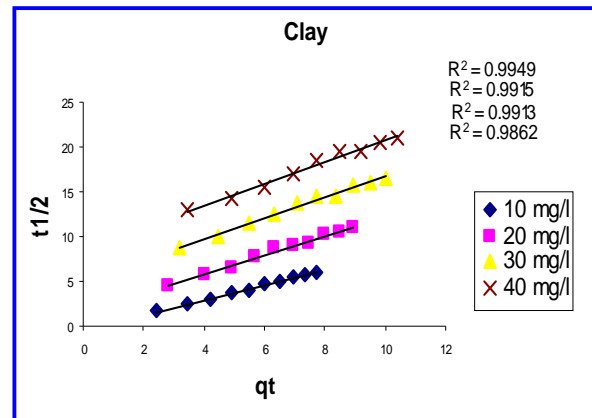


Fig. 22: Weber-Morris Intraparticle Diffusion model of Fire Clay

3.8 Thermodynamic parameters

The thermodynamic parameters for the adsorption process such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated using the following equations:

$$\ln K_C = \Delta S^\circ / R - \Delta H^\circ / RT \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(8)

Where K_C is the Langmuir constant related to the energy of adsorption, R is the gas constant and T is the absolute temperature (K). The values of ΔH° and ΔS° can be calculated, respectively, from the slope and intercept of the Van't Hoff plot of $\ln K_C$ versus $1/T$.

The calculated values of ΔH° , ΔS° and ΔG° for adsorption of Pb(II) on both nanocomposite and clay were given in Table 3. Positive values of ΔH° confirms that the adsorption process to be endothermic. The negative value of ΔG° at various temperatures indicates the feasibility and spontaneity of the adsorption process. The positive value of ΔS° shows the affinity of adsorbent for Pb(II) and it further confirms a spontaneous increase in the randomness at the solid- solution interface during the adsorption process.

3.9 Desorption studies

Desorption studies with acetic acid revealed that the regeneration of adsorbent was not satisfactory, which confirms the chemisorptive nature of adsorption.

4. CONCLUSION

This study shows that the Fire Clay and nanocomposite can be used effectively in the removal of Pb(II) through adsorption. Both clay and nanocomposite followed Langmuir, Freundlich, D-R, fairly fitted with Tempkin, Harkin-Jura and Halsey models. Pseudo second order kinetic model was followed. The sorption suggested that the adsorption is high at basic medium. Elkovich kinetic model suggested that adsorption process is chemisorptive nature. The adsorption also followed by intraparticle diffusion model. The calculated values of different thermodynamic parameters clearly indicated that the adsorption process with nanocomposite and clay was feasible, spontaneous and exothermic nature. This study also reveals showed that Fire Clay-TiO₂ nanocomposite exhibited higher adsorption capacity when compared to Fire Clay in its natural form.

REFERENCES

- Babu, B. and Ramakrishnan, V., Ranking of adsorbents based on method of preparation and isotherm Freundlich. In proceedings of the International Symposium 56th Annual Session of II ChE(Chemcon-2003), Bhubaneswar., 19-22(2003).
- Ho, Y. S. and McKay, G., Pseudo- Second order Model for sorption processes, *Process Biochem.*, 34(5), 451-465(1999).
[doi:10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5)
- Karthikeyan, G., Anitha pius. and Alagumuthu, G., Fluoride adsorption studies of montmorillonite clay, *Ind. J. Chem. Technol.*, 12, 263-272(2005).
- Kobya, M., Demirbas, E., Senturk, E. and Ince, M., Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresources. Technol.*, 96(13), 1518-1521(2000).
[doi:10.1016/j.biortech.2004.12.005](https://doi.org/10.1016/j.biortech.2004.12.005)
- Langmuir, I., The Constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.*, 38, 2221-2295(1916).
[doi:10.1021/ja02268a002](https://doi.org/10.1021/ja02268a002)
- Mall, I. D., Srivastava. V. C., Agarwal, N. K. and Mishra, I., Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis, *Chemosphere*, 61(4), 492-501(2005).
[doi:10.1016/j.chemosphere.2005.03.065](https://doi.org/10.1016/j.chemosphere.2005.03.065)
- Mehmet Doğan, Mahir Alkan and Yavuz Onganer, Alkan, Y. and Onguner, Adsorption of methylene blue on perlite from aqueous solutions, *Water, Air and Soil Pollution*, 120(3), 229-248(2000).
[doi:10.1023/A:1005297724304](https://doi.org/10.1023/A:1005297724304)
- Norrozi, B, Sorial, G. A., Bahrami, H. and Arami, M., Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent-silkworm pupa, *J. Haz. Mat.*, B, 139, 167-174(2007).
[doi:10.1016/j.jhazmat.2006.06.021](https://doi.org/10.1016/j.jhazmat.2006.06.021)
- Ozcan, A. S., Erdem, B. and Ozcan, A., Adsorption of acid blue 913 from aqueous solutions onto BTMA-bentonite , *Colloid surface A.*, 266, 73-81(2005).
- Öztürk, A. and Malkoc, E., Adsorptive potential of cationic Basic Yellow 2 (BY2) dye onto natural untreated clay (NUC) from aqueous phase: Mass transfer analysis, kinetic and equilibrium profile, *Applied Surface Sci.*, 299, 105 -115(2014).
[doi:10.1016/j.apsusc.2014.01.193](https://doi.org/10.1016/j.apsusc.2014.01.193)
- Parimaladevi, P. and Venkateswaran, V., Kinetics, thermodynamics and isothermal modeling of adsorption of triphenyl methane dyes (Methyl violet, Malachite green and Magenta-2) onto fruit waste, *J. of Appl. Tech. in Environmental Sanitation* 1(3), 273-283(2011).
- Weber, W. J. and Morris, J. C., Preliminary appraisal of advanced waste treatment process, *Proc. Int. Conf., Advances in Water Poll. Res.*, 2, 231-241(1963).